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The Study on the Fixation of Cs-137 Radionuclide in Clinoptillolite

— The Fixation of Cesium in Clinoptillolite —

Sang Hoon Lee, Nak June Sung, Won Jong Park

Division of Radioactive Waste Management, Korea Atomic Energy Research Institute

Seoul, Korea

—ABSTRACT—

Investigation is carried out that low-level liquid radioactive wastes which is consisted of long half-life nuclides such as cesium can be treated by Korean clinoptillolite as a kind of zeolites.

Column operation using a activated clinoptillolite shows good results in terms of break-through curves and comparing to clinoptillolite classified at WARD in U.S, Korean clinoptillolite shows a tailing phenomena longer than that of WARD.

The fixation quantity of radioactivity in Korean clinoptillolite is to be about 75μCi/100g using a $2.5\times10^{-3}\mu$Ci/ml solution.

1. Introduction

The liquid wastes produced at nuclear power plant have been treated to decontaminate in various ways the radionuclides dissolved in it.

The accidental and purposeful release of such fission fragments into the environment is harmful to all lives.

Of particular importance is cesium ions due to the combination of abundance and relatively long half-lives. A research[1] has been made to determine which clayminerals will selectively absorb the cesium. It is well known that natural clayminerals have a sorption capability of various metal cations. In veview of the sorption study of radioabtive elements. S. J. Rimshaw[2] et al. carried out the removal efficienies of series of minerals considering exchangeable capacity of nuclides on various minerals such as Marble chips, pebble phosphate and natural soils.

This study covered almost all of the clayminerals so that it defected the detail something to a certain clayminerals. The zoelites also have been used for the removal of fission products in the laboratory. L. L. Ames[3] showed that clinoptillolite which is a kind of zeolites has excellent removal efficiency for the cesium.

And clinoptillolite has been used in mineralization processes for the high level radioactive wastes containing most of actinides and fission products.[4] In the previous paper[5] the study on the cation exchange capacity(CEC) using about 20 kinds of clayminerals, it was confirmed that the CEC of clinoptillolite is higher than that of other clays. Although clinoptillolite is inferior to the synthetic ion exchanger in terms of pure exchange capacity, it will be able to treat the liquid effluents containing low-level radioactivity produced at steam generator* blowdown or dirty wastes at floor drains and laundary in nuclear power plant.

The purpose of this study is to investigate mimeralization or a possible method of decontamination of cesium using Korean clinptillolite which the resource is assumed almost infinite quantity.

The present paper demonstrates the fixation of cesium in Korean clinoptillolite in terms of break-through curve which is obtained by column operation and compare its characteristics to clinoptillolite classified at Wards' National Science Estabilishment, Rochester, N.Y.

2. Experiment

Clinoptillolite has one very distinct advantage over montmorillonite or vermiculite. This is the mechanical stability of the small chunks when exposed to an electrolyte solution. The material being 20 mesh can be placed directly in a column. A steady flow rate can be maintained. There is no tandency for the column to clog even in the electrolyte solutions. Other clays such as montmorillonite and vermiculite can not be used in a column in the presence of electrolyte solutions. Clinoptillolite has a tremendous advantage in that it can be used in the column and will allow a large variation in flow rate. Clinoptillolite used in this experiment is obtained from Wards' National Science Estabilishment and from Young IL Gun, Kyoung Sang Nam Do in Korea.

Clinoptillolite was grounded and sized to 20 mesh which was proved to the optium size in the preliminary test for the column operation. A known quantity of clinoptillolite was mixed

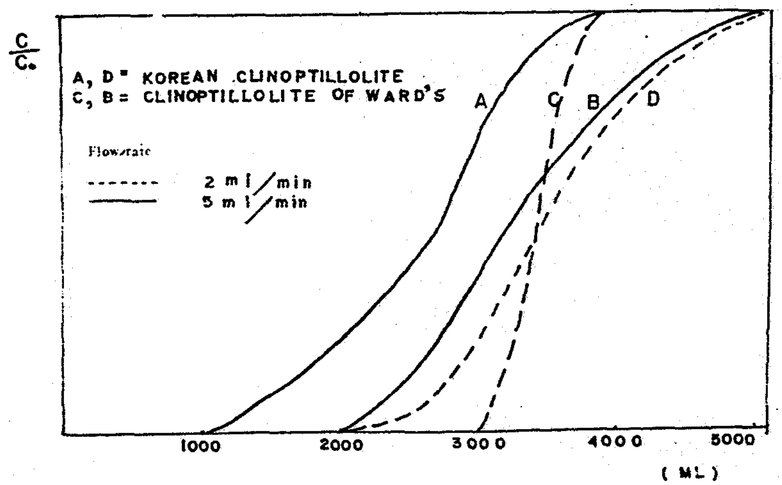

Fig. 1. Break-Through Curves of Cs^+ in Clinoptillolite
C_0: initial concentration of solution C: concentration of effluents

with sodium oxalate solutions for two hour at a temperature of 60—70°C. This process is called saturation process or activation process. After this saturation with sodium ion, clinoptillolite was washed with distilled water in three times and then packed in the column.

* The discharge from steam generator blowdown in nuclear power plant is usually not treated since the radioactivity per ml is not detected in normal operation. However, the total amounts during a year or life time of nuclear power plant is very large volume so that the quantity of nuclides in that is not negligible.

The saturation and elution for the sorption of cesium ions in clinoptillolite were determined at room temperature. This was done by taking a column containing 10 gr. of clinoptillolite and elution with 500 ppm cesium chloride with the radioistope cesium-137 added. The radioactivity in solution is to be $2.5\times10^{-3}\mu Ci/ml$. The sorption of cesium ion shows the concentration of the effluent as a function of the volume of solution through the column.

When the concentration of the effluent rose to and remained equal to the concentration of the input solution, the sorption was complete. The exchange capacity of the clinoptillolite is then just equal to the total quantity which entered the column and not bound in the effluent.

This "uptake or sorption" can be determined quantitatively from the area over the break through curve. The results are graphed in Fig. 1. The pH of the solution is 7.8—8.5. The fractions of each effluents are separated as 10 ml and counted by BAIRD-ATOMIC scintillation counter.

Each 10 ml fraction of effluent is separated by fraction collector made in ISCO.

The column diameter is 2.5 cm and the length is 30 cm. Each connection part is connected by joints to prevent the leakage of radioactivity.

3. Results

The break-through curves represented in Fig. 1 are obtained in variance with the flow rate in a range of 2 ml/min. and 5 ml/min. The same condition is applied for the Korean and Wards' clinoptillolites. The nature of the natural clinoptillolite means that all the exchange positions are not equally rapidly available to ions in solutions.

Considering these phenomena, the extension of contact time between clinoptillilite and solution will make the exchange capacity increased. The Figure shows that the break-through curve is dependent sensitively on the change of flow-rate.

Korean clinoptillolite shows almost the same capacity compared to the clinoptillolite classified by WARD. But Korean clinoptillolite has a tailing phenomena longer than that of WARD. It may be interpreted at persent that clinoptillolite taken in Young IL Gun contains impurities such as feldspar, quartz and montmorillonite. *[5] It will be analyzed the purity of clinoptillolite using X-ray diffraction and DTA in next paper. The CECs of montmorillonite and feldspar are lower than that of clinoptillolite as much as one third in the study of CEC which described in previous paper.[6]

The total quantity trapped at 2ml/min is 132 meq/100g in Korean clinoptillolite and 135meq/100g in clinoptillolite classified by WARD. Although the total quantity trapped in both clinoptillolites is almost equal, there is a difference in terms of the pattern of break-through curves.

There is no radioactivity in the effluents until about 3000ml passed through the column as a rate of 2ml/min in case of WARD clinoptiltolite and sharp increase of radioactivity in effluents is shown after the first leakage occurs. However, clinoptillolite taken from Young Il Gun does not show the sharp curve. This fact means that natural clinoptillolite in Young Il Gun be purified for the application in the treatment of radioactive nuclides in liquid wastes.

4. Discussion

The zeolites framework is open and wide

* It was cited from the contents reported at the Zeolite Symposium in the Korean Chemical Society, 1978.

Table 1. Data on Hydration of Aqueous Group 1 ions

	Li^+	Na^+	K^+	Rb^+	Cs^+
Crystal radii, Å	0.86	1.12	1.44	1.58	1.84
Hydrated raddi(approx), Å	3.40	2.76	2.32	2.28	2.28
Approximate Hydration Numbers	25.3	16.6	10.5	—	9.9
Hydration Energy, KJ mol^{-1}	519	406	322	293	264
Ionic mobilities(at ∞ dilly 18°C)	33.5	43.5	64.6	67.5	68

meshed with cavities containing cations to balance the negative charge of the framework. The diameter or window of clinoptilite is to be about 4.3Å.[7] The hydrated radii of cesium is approximately is known about 2.28Å.[8] The ion-exchange mechanism between Na^+ and Cs^+ is assumed to be interpretated as follows. It is quite possible that Cs^+ might have six water molecules in the first hydration shell. However, electrostatic forces are still operative beyond the first hydration sphere, and additional water molecules will be bound in layers of decreasing definiteness and strength of attachment. Apparently, the cation itself, the less it binds additional outer layers, so that, although the crystallographic radii increase down the group, the hydrated radii decsease as shown in Table 1.[7] The mobility of the ions in electrolytic conduction increases, and so generally does the strength of binding to ion-exchange materials.

In a cation-exchange process, two cations compete for attachment at sites of negative charge in the cavities in zeolites, as in the following equilibrium:

$$Cs^+(aq) + [Na^+R^-](s) = Na^+(aq) + [Cs^+R^-](s)$$

Where R represents the zeolite cavity.

Such equilibria have been measured quite accurately, and the order of preference of the alkali cations is usually $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, although irregular behavior does occur is some modes.

The usual order may be explained if we assume that the binding force is essentially electrostatic and that under ordinary conditions the ions within the water-logged cavity are hydrated approximately as they are outside it.

Then the ion with the smallest hydrated radius(which is the one with the largest "naked" radius) will be able to approach most closely to the negative site of attachment and will hence be held most strongly according to the coulomb law.

The reasons for the deviations from this simple pattern as well as selective passage of certain ions through cell walls are not properly understood, and factors other than mere size are doubtless important. The other factors which can vary the CEC in clinoptillolite is assumed species of the counter anions of salts used in the saturation of it. We used sodium oxalate which the oxalate anion can chelate cesium ion effectively. It will be demonstrated effects of counter anions on ion-exchange mechanism in next paper.

5. Conclusions

The following conclusions can be drawn from this study.

1) Clinoptillolite taken at Young Ill Gun showed the fixation capacity about 75μCi/100g using 500ppm cesium chloride solution which the radioactivity was adjusted to $2,5\times10^{-3}$μCi/ml with $^{137}CsCl$.

2) The quantity of Cs^+ trapped in clinoptill-

olite is to 132meq/100g.

3) Column operation using clinoptillolite can be used for the decontamination of the low-level liquid radwaste effectively.

6. References

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—抄　錄—

Clinoptillolite에 依한 Cs-137 核種 吸着에 關한 研究

李相薰 · 成樂俊 · 朴元鍾

韓國原子力研究所

Cs-137과 같은 반감기가 긴 방사성 핵종을 함유한 저준위 방사성 액체 폐기물을 국산 제올라이트 일종인 Clinoptillolite를 이용해서 처리할 수 있는가를 연구했다.

Column 장치를 사용하여 Break-Through Curve를 얻어서 미국의 광물전문회사인 WARD에서 분류한 천연 Clinoptillolite 원광과 비교한 결과, 국산 Clinoptillolite에는 Break-Through Curve의 모양에 "Tailing"이 일어나는 것을 나타냈다. 국산 Clinoptillolite에 500ppm의 Cesium 용액에 $2.5\times10^{-3}\mu Ci/ml$의 Cs-137을 넣어서 Cesium 이온고정능력을 실험한 결과 132meq/100g이 고정되었다. 또한 Tracer로 넣은 Cs-137이 $75\mu Ci/100g$이 고정됨을 보여주었다.